Reticular Chemistry of Metal–Organic Polyhedra

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In memory of F. Albert Cotton (1930–2007)
Metal–organic polyhedra (MOPs), are discrete metal–organic molecular assemblies. They are useful as host molecules that can provide tailorable internal volume in terms of metrics, functionality, and active metal sites. As a result, these materials are potentially useful for a variety of applications, such as highly selective guest inclusion and gas storage, and as nanoscale reaction vessels. This review identifies the nine most important polyhedra, and describes the design principles for the five polyhedra most likely to result from the assembly of secondary building units, and provides examples of these shapes that are known as metal–organic crystals.

1. Introduction

Reticular chemistry\(^{[1]}\) is concerned with the design and synthesis of compounds formed from finite secondary building units (SBUs) joined by strong chemical bonds. A basic premise, amply supported by experimental data,\(^{[2]}\) is that when symmetrical SBUs are joined by simple linkers (“struts”) only one of a small number of known, high-symmetry, structures will be formed.\(^{[3, 4]}\) A valuable aspect of this approach is that knowing what structures to expect can facilitate unambiguous determination of the structure of complex crystals for which only limited powder X-ray diffraction data are available.\(^{[5]}\) In the most highly developed part of this discipline, that of metal–organic frameworks (MOFs), there are usually two components: a metal-containing, formally cationic, part and an organic, formally anionic, part that combine to produce an often neutral framework. The ability to synthesize predetermined MOF structures allows unprecedented freedom to design porous materials for specific purposes.\(^{[6]}\)

In structures with ditopic organic linkers there will generally be just one kind of inorganic SBU and one kind of link. The nets describing the underlying topology of these structures have just one kind of vertex and one kind of edge—in the jargon they are vertex- and edge-transitive. They have been categorized as regular, quasiregular, and semiregular. We know of just 20 of such nets which have the property that they have embeddings in which there is no inter-vertex distance shorter than the edge length.\(^{[7]}\)

More generally there will be polytopic organic and inorganic SBUs and now the important (default) nets will have two kinds of vertex and one kind of edge. Edges of course link unlike vertices, and we have found that with the restriction that there is an embedding in which no distance between unlike vertices is shorter than an edge length, there are 34 of these.\(^{[8]}\) They include the nets of most relevance to reticular chemistry.

Instead of frameworks, one can synthesize what we have termed metal–organic polyhedra (MOPs), the main subject of this review.\(^{[9]}\) Now the SBUs will be topological polygons (we give numerous examples below) and we ask for the ways of linking polygons by one kind of link to form closed structures (“polyhedra”). We will describe the nine such basic structures below. We will then illustrate the principles of their realization in molecules with a number of selected examples. This work is not intended to replace the several excellent recent reviews of polyhedral molecules, particularly by pioneers in the field.\(^{[10]}\) Rather it is intended to provide and illustrate a firm conceptual basis for the design and synthesis of such materials.

2. Edge-Transitive Polyhedra

We remark first that it has been known since antiquity that the vertex-transitive polyhedra comprise the five regular (Platonic) solids, which are also edge- and face-transitive, and the Archimedean solids. Of the latter there are two (the quasiregular polyhedra) that are also edge-transitive, but
which have two kinds of face. The duals\textsuperscript{[13]} of the regular polyhedra are necessarily regular polyhedra. The duals of the two quasiregular polyhedra are edge- and face-transitive but have two kinds of vertex. It is easy to see that this enumeration is complete.\textsuperscript{[12,13]}

In Figure 1 we illustrate these nine polyhedra. They include the familiar regular solids (first row in the figure) and the quasiregular polyhedra, the cuboctahedron and icosidodecahedron. The duals of these last two have two kinds of vertex, but one kind of face and are examples of Catalan polyhedra. The polyhedra often have cumbersome names and we find it convenient to refer to them by their three-letter RCSR symbols such as \textit{ido} for icosidodecahedron.\textsuperscript{[14]} The polyhedra with symbols \textit{ico}, \textit{dod}, \textit{ido}, and \textit{trc} have icosahedral symmetry; the remaining five are cubic.

Also shown in Figure 1 are the polyhedra obtained by replacing the original vertices by a polygon with the number of sides equal to the valence of those vertices. This process of generating related polyhedra is usually referred to as \textit{truncation}, as the new polyhedra can be considered derived from the original ones by slicing off the original vertices, but as we want to extend the process to infinite nets, we prefer the term \textit{augmentation}.\textsuperscript{[3]} If the original structure has symbol \textit{xyz}, we often write the symbol of the augmented version as \textit{xyz-a}.

These nine augmented polyhedra represent the nine ways of linking polygons with one kind of link to form closed shapes and are the focus of this review.\textsuperscript{[15]} As may be seen from Figure 1 the polygons may have three, four, or five vertices and will be realized by SBUs that have three, four, or five \textit{points of extension} (linking sites).

The polyhedral molecule may be either composed of one kind of SBU linked by a ditopic linker, or of two SBUs with more than two points of extension. An SBU with \textit{n} points of extension is referred to as \textit{n}-valent. In the following sections we will focus particularly on the cases with cubic symmetry as there are few, if any, icosahedral molecules that are built up
from SBUs and for which there are atomic coordinates. The case of the cube is special (it is the only regular polyhedron with even-sided faces). With one kind of link it can correspond either to eight identical SBUs linked by a ditopic linker, or to four SBUs of one kind (say cationic) linked to four SBUs of a different kind (anionic). In the latter case we call it a heterocube.

3. SBUs and linkers

There are two important angles that characterize the geometry of an assembly. The first is the angle $\eta$ between the links from the SBU (Figure 2). The second is the angle $\theta$ between the links of a ditopic linker (Figure 3). We give some examples of special cases because the first task of the designer and would-be synthesizer is to design SBUs and linkers of the correct geometry for the required product.

![Figure 2. Examples of SBUs: a) Two Mn centers (pink) bridged by three carboxylates (C black, O red), with terminal solvent ligands on each Mn center (red spheres); b) two Cu centers (blue) bridged by four carboxylates, with a terminal solvent ligand on each Cu center; c) three Fe centers (light blue) bridged by three carboxylates, with capping sulfate groups (S yellow). Below (a) through (c) are the corresponding polygons highlighting the angle $\eta$ between the coordination vectors of the links. The green polygons are constructed between the points of extension of the inorganic cluster. d,e) Examples of organic SBUs (C black, N green) and the corresponding coordination vectors.

![Figure 3. Examples of linkers with angle $\theta$ between links. Linkers can be organic, as in (a) and (b), or inorganic, such as the capped Mo cluster in (c), in which the shape of the cluster, including two bulky aminidinate capping (cap) ligands, is described by the green square. The color scheme is the same as in Figure 2 (Mo = blue).

4. Molecules Based on the Tetrahedron

Here we have four trivalent SBUs with links at an angle $\eta$ joined by ditopic linkers bent at an angle $\theta$. Two extreme cases, $\eta = 60^\circ$, $\theta = 180^\circ$ and $\eta = 120^\circ$, $\theta = 70.5^\circ$ are shown in Figure 4. An intermediate case $\eta = \theta = 109.5^\circ$ corresponds to the vertices of an adamantane cage. In general if we set $x = \sin(\eta/2)$ and $y = \sin(\theta/2)$, $4x^2 - 4xy + 3y^2 = 2$.

![Figure 4. Two configurations of four trivalent SBUs linked to form a tetrahedron.

The first extreme case is represented by IRMOP-51 (Figure 5), which is composed of sulfate-capped basic iron carboxylate trimer cluster SBUs connected by biphenyl linkers. The iron carboxylate cluster has three of its six points of extension capped by sulfate ligands, leaving three points of extension with $\eta = 68.7^\circ$, and the biphenyl linker is almost linear ($\theta = 175.9^\circ$). IRMOP-50, -52, and -53 share the same geometry, with different linear linkers: benzene, tetrahydrophenyl, and terphenyl, respectively, instead of biphenyl.

The second extreme case is illustrated in Figure 6. In this case, we consider $\eta$ as the average of the angles between points of extension for the T-shaped, mono-capped Mo paddle-wheel (two of 90°, one of 180°), so $\eta = 120^\circ$. In addition, we consider $\theta$ as the average of the six thiophene-3,4-dicarboxylate linkers (four linkers of 73.1° and two of
65.7°), thus θ = 70.6°. This molecule exhibits a large deviation from ideality, accommodated in the assembly by distorting the underlying tetrahedral shape and lowering the point group symmetry from $T_d$ to $D_3$. An essential element of this distortion is the twisting of carboxylate groups out of the thiophene plane (the torsion angles are: 56.0° and 1.2° for one type of linker; 33.4° and 33.4° for the other), as shown in Figure 6.

Another example of tetrahedral construction of the second extreme case, with organic SBUs and inorganic linkers, is composed of 1,3,5-benzenetricarboxylate (btc) SBUs linked by capped Mo paddle-wheel squares (Figure 7, η = 120°, θ = 83.4°). The rigidity of btc limits any adjustments to η; instead, angular tuning to form the structure comes from the non-ideal coordination of the carboxylate groups to the capped Mo dimer cluster.

A third tetrahedral compound close to the second extreme case, again with organic SBUs and inorganic linkers is shown in Figure 8 (η = 118.7° and 120°, θ = 84.8° and

![Figure 5. An example of a tetrahedron in the first extreme case.](image)

![Figure 6. An example of a tetrahedron close to the second extreme case.](image)

![Figure 7. The tetrahedral cage formed by btc SBUs (η = 120°) linked by capped Mo paddle-wheels (θ = 83.4°).](image)

![Figure 8. a) The tetrahedral cage [(bpy)$_6$Pd$_6$(tpt)$_4$]$^{2+}$ (bpy = 2,2'-bipyridine, tpt = 2,4,6-tris(4-pyridyl)-triazine); b) the top view and c) the side view of one tpt SBU observed in the tetrahedral assembly.](image)
The proposed structure of a molecule of the special situation \( \eta = \theta = 109.5^\circ \) of a tetrahedron; the structure was proposed on the basis of NMR evidence. The organic SBUs, with sp\(^3\)-hybridized C centers, are linked to the organoplatinum links, which also have sp\(^3\)-hybridized C centers. Two phosphine ligands on each Pt center are omitted for clarity. (Pt purple, C black, N green, OH red).

We first note the lack of an example for the first extreme situation, probably due to the scarcity of tetravalent metal SBUs with an angle \( \eta = 60^\circ \).

The first example of the second extreme situation (\( \eta = 90^\circ, \theta = 90.0^\circ \)) is MOP-28 (Figure 11).\(^{27}\) The Cu paddle-wheel is slightly distorted but maintains an average angle \( \eta \) of 90.0°. The paddle-wheel is connected by 2,2′:5,2′-terthio-

\[ \eta = 82.2^\circ, \theta = 120^\circ.\]^{28} The points of extension are the C atom of the carboxylate group at the 5-position and the N atom of the 2,5-pyridinedicarboxylate linker (the carboxylate at the 2-position is irrelevant for topological analysis). Therefore, the linker has an angle \( \theta = 120^\circ \) and the geometry of the metal SBU deviates from square planar, \( \eta = 90^\circ \). When \( \theta = 120^\circ \), the general relation between \( \eta \) and \( \theta \) for this construction type gives \( \eta = 86.2^\circ \). The calculation shows that a large deviation in \( \theta \) of the ditopic linker (120°−90° = 30°) can be accommodated by a small deviation in \( \eta \) of the square metal SBU (90°−86.2° = 3.8°). The capability of the relatively flexible single metal ion vertex to tune \( \eta \) is the key to this construction.
6. Molecules Based on the Cube

Here we have eight trivalent SBUs with links at an angle $\eta$ joined by ditopic linkers bent at an angle $\theta$. Two extreme cases, $\eta = 90^\circ$, $\theta = 180^\circ$ and $\eta = 120^\circ$, $\theta = 109,5^\circ$ are shown in Figure 13. In general if we set $x = \sin(\eta/2)$ and $y = \sin(\theta/2)$, $4x^2 - 4\sqrt{2}xy + 3y^2 = 1$.

![Figure 13. Two configurations of eight trivalent SBUs linked to form a cube.](image)

Figure 13. Two configurations of eight trivalent SBUs linked to form a cube.

Figure 14 illustrates an example of the first situation with a structure based on NMR evidence. The capped Ru SBUs have angle $\eta = 90^\circ$ imparted by the octahedral coordination environment. The SBUs are connected through linear 4,4'-bipyridine linkers ($\theta = 180^\circ$).

![Figure 14. An example of the construction of a cube. The model of the simple cubic structure $[\text{L}_8\text{Ru}_8(\text{bpy})_{12}]^{16+}$ (L = 1,4,7-trithionane; bpy = 4,4'-bipyridine) proposed based on NMR evidence. (Ru blue, C black, N green, S yellow).](image)

Figure 14. An example of the construction of a cube. The model of the simple cubic structure $[\text{L}_8\text{Ru}_8(\text{bpy})_{12}]^{16+}$ (L = 1,4,7-trithionane; bpy = 4,4'-bipyridine) proposed based on NMR evidence. (Ru blue, C black, N green, S yellow).

Another example of the first extreme case is shown in Figure 15 ($\eta = 96.0^\circ$, $\theta = 176.2^\circ$). The points of extension are the N atoms of the 4,5-imidazolodiacarboxylate linkers (Figure 15a and b, in green). The chelation of this linker to Ni$^{2+}$ centers has rendered Ni-Im-Ni almost linear, giving rise to an angle $\theta$ close to $180^\circ$ (Figure 15b, in green).

Significantly, this example can be viewed in comparison with the second extreme case ($\eta = 120^\circ$, $\theta = 109.5^\circ$), if one uses the centroids of the chelating units as points of extension instead of the N atoms on the imidazole ring. Consequently the metal SBUs are now planar triangles with $\eta = 120^\circ$ and the angle $\theta$ of the linker is $92.3^\circ$ (Figure 15b and c, blue vectors and grey triangle, respectively). The observed $\theta$ shows a large deviation from the expected $109.5^\circ$. This is because the points of extension do not orient toward the edge-centers, as assumed in deriving the general relation between $\eta$ and $\theta$ for this construction type. The N atoms of the linker orient toward the edge-centers of the Ni$_8$ cube and they define the ideal orientation (Figure 15c, green triangle). A rotation of the triangle defined by the centroids of the chelating units (Figure 15c, grey triangle) from the ideal orientation by $23^\circ$ is responsible for the observed large discrepancy in $\theta$ ($109.5^\circ - 92.3^\circ = 17.2^\circ$).

7. Molecules Based on the Cuboctahedron

Here we have twelve tetravalent SBUs joined by ditopic linkers. Two extreme cases are shown in Figure 16. Notice that, as the tetravalent SBUs are not at sites of fourfold symmetry, there are no longer simple expressions relating the

![Figure 15. An example of the construction of a cube. a) The cubic cage composed of eight Ni$^{2+}$ centers and twelve 4,5-imidazolodiacarboxylate linkers. b) The 4,5-imidazolodiacarboxylate linker whose coordination vectors depend on the choice of points of extension: green arrows using the N atoms; blue arrows using the centroids of C–C bonds of the NCCO$^-$ chelating units. c) The [Ni(NCCO)$_3$]$^-$ SBU whose shape depends on the choice of points of extension: green triangle using the N atoms; gray triangle using the centroids of C–C bonds of the NCCO$^-$ chelating units. (Ni blue, C black, N green, O red).](image)

Figure 15. An example of the construction of a cube. a) The cubic cage composed of eight Ni$^{2+}$ centers and twelve 4,5-imidazolodiacarboxylate linkers. b) The 4,5-imidazolodiacarboxylate linker whose coordination vectors depend on the choice of points of extension: green arrows using the N atoms; blue arrows using the centroids of C–C bonds of the NCCO$^-$ chelating units. c) The [Ni(NCCO)$_3$]$^-$ SBU whose shape depends on the choice of points of extension: green triangle using the N atoms; gray triangle using the centroids of C–C bonds of the NCCO$^-$ chelating units. (Ni blue, C black, N green, O red).
angles. If there are straight linkers and the SBU centers are at
the vertices of a cuboctahedron (Figure 16, right), then there
are two angles (60° and 90°) between the links from the center
of the SBU. If the SBU is square with 90° between links
(Figure 16, right) then the ditopic linker must be bent at an
angle of 117° (it is important that this is close to 120°).

Figure 17a shows the structure of MOP-1, an example of
this construction type composed of a Cu paddle-wheel SBU
($\eta = 90^\circ$) and a 1,3-benzenedicarboxylate linker ($\theta = 120^\circ$).[9]
Another good example is shown in Figure 17b; in this

The first extreme case of heterocube formation ($\eta_1 = \eta_2 =
90^\circ$) is represented by a metal cyanide cage shown in
Figure 19 ($\eta_1 = 93.6^\circ$, $\eta_2 = 91.5^\circ$).[35] The four
{Co(H$_2$O)$_3$(CN)$_3$} centers are assigned $\eta_1$, whereas the four
{Co(tach)(CN)$_3$} units are assigned $\eta_2$ (tach = cis,cis-1,3,5-
triaminocyclohexane). This assignment is consistent with the
synthetic approach and the intrinsic tetrahedral symmetry of
this cage. If both types of Co centers are counted as vertices,
this structure represents construction of a heterocube.

A good example of the second extreme case ($\eta_1 = 120^\circ$,
$\eta_2 = 33.6^\circ$) is shown in Figure 20.[36] The first of the two SBUs,
the trithiocyanurate unit, has $\eta_1$ of 120° (Figure 20a). The

structures Pd$^{2+}$ centers are linked by 2,5-bis(4-pyridyl)furan
linkers ($\eta = 90^\circ$, $\theta = 122.8^\circ$) to afford the cuboctahedral
assembly.[31]

Fujita and co-workers have reported similar examples of
cuboctahedra, including examples with pyridyl groups meta
to each other on benzene rings ($\theta = 120^\circ$) and with pendant
groups directed either into or out of the cage, sometimes
referred to as a “sphere.”[32–34]

8. Molecules Based on the Heterocube

Here we have two trivalent SBUs with links at an angle $\eta_1$
and $\eta_2$. We assume that they are joined together so that the
links from two joined SBUs are colinear. Two extreme cases,
$\eta_1 = \eta_2 = 90^\circ$, and $\eta_1 = 120^\circ$, $\eta_2 = 33.6^\circ$ are shown in Figure 18.
In general if we set $x = \sin(\eta_1/2)$ and $y = \sin(\eta_2/2)$, $3x^2 - 4xy +
3y^2 = 2$.
second SBU, with $\eta_2$ of 35.6°, is composed of the Zn$_3$L unit (L = 1,3,5-tris-(1,4,7,10-tetrazacyclododecan-1-ylmethyl)benzene) (Figure 20b), connected to the first SBU by Zn–S bonds. The Zn equatorial coordination sites are all occupied by the macrocycle ligand of the second SBU, leaving only the apical positions open for the S atoms of the trithiocyanurate SBU to coordinate.

MOP-54 is an example of the second extreme case wherein large deviations from the special angles occur ($\eta_1 = 109°$, 115°, 116°, $\eta_2 = 65.2°$, 67.9°, 68.3°; Figure 21). Interestingly, the observed $\eta_1$ and $\eta_2$ of MOP-54 actually fit into the general equation well. When $\eta_2 = 67.1°$ (the average of the observed values of $\eta_2$), the equation gives $\eta_1 = 108.7°$.

The calculation shows that, in the ($\eta_1$, $\eta_2$) region under investigation, a large difference in $\eta_2$ (67.1°–33.6° = 33.5°) can be compensated by a relatively small change in $\eta_1$ (120°–108.7° = 11.3°) due to the property of the function itself. The large triangular linker 1,3,5-benzentribenzoate (btb) distorts to accommodate the required angle $\eta_1$ (Figure 21b and c). The remaining discrepancy in $\eta_1$ is addressed by the distorted Fe-carboxylate coordination linkage.

9. Molecules Based on the Rhombic Dodecahedron

Here we have eight trivalent SBUs and six tetravalent SBUs with links at an angle $\eta_1$ and $\eta_2$, respectively. We assume that they are joined together so that the links from two joined SBUs are colinear. There are now three extreme cases: a) $\eta_1 = 120°$, $\eta_2 = 48.2°$, b) $\eta_1 = 109.5°$, $\eta_2 = 70.5°$, c) $\eta_1 = 60°$, $\eta_2 = 90°$ (Figure 22). In general if we set $x = \sin(\eta_1/2)$ and $y = \sin(\eta_2/2)$, 2$x^2 - 2\sqrt{2}xy + 3y^2 = 1$. In case (b) the vertices are at the positions of the vertices of an ideal rhombic dodecahedron. In case (a) the trivalent vertices are in the faces of an octahedron of the tetravalent vertices, and this configuration is often referred to, we think wrongly, as an octahedron. In case (c) the tetravalent vertices are in the faces of a cube of the trivalent vertices, and this configuration is often referred to, again we think wrongly, as a cube.

We are not aware of any reported structure illustrating the special case (b).

Figure 23 shows a MOP structure of extreme situation (a), constructed from pyrogallol[4]arene units coordinated to copper through its oxygen atoms to form Cu$_3$O$_3$ triangles. The large cone-shaped pyrogallol[4]arene SBU has an angle $\eta_1 = 42.2°$, whereas the planar Cu$_3$O$_3$ SBU has an angle $\eta_1 = 120°$.

The [(Me$_3$tacn)$_8$Cr(CN)$_2$]$_{12+}$ cage shown in Figure 24 ($\eta_1 = 88.1°$, $\eta_2 = 89.1°$) is an interesting example to compare with extreme situation (c). The geometry of the [Ni(CN)$_2$]$_{12-}$ SBU is very close to square planar ($\eta_2 = 89.1°$), but the angle $\eta_1$ of the (Me$_3$tacn)Cr(CN)$_2$ SBU deviates from the expected value greatly (88.1°–60° = 28.1°). Figure 24b shows how this structure can form with such large deviation in $\eta_1$. The
coordination vectors of the Ni SBU (blue arrow) and the Cr SBU (pink arrow) are not colinear, and have a significant angle between them (the supplement of the bond angle C-N-Cr: \(180^\circ - C_0 = 119.0^\circ\)).

Another example of extreme situation (c) is shown in Figure 25 (\(h_1 = 90^\circ, h_2 = 55.6^\circ\)). The 1,3,5-tris(4-pyridylmethyl)benzene SBU in this particular conformation is very useful in that it adopts an angle \(\eta_1\) close to \(60^\circ\).

10. Summary of Deviations

All of the above examples exhibit some degree of deviation from the angles calculated for extreme situations. The factors contributing to the tolerance for the deviations in MOPs from the special angles can be summarized into two categories according to the applicability of the general relations between the angles \(\eta\) and \(\theta\) to the structures under question: small deviations in one angle (<\(10^\circ\)) and large deviations in one angle (>\(10^\circ\)).

As has been detailed above, small deviations in one of the two angles (<\(10^\circ\)) are generally within a tolerance level that the other angle does not need adjustment. Large deviations in one angle are accommodated by small deviations in the other angle: the second angle is always close to what is calculated to be the accommodating angle based on the equation appropriate for the polyhedron, as is seen in three of the four molecules with significant deviation.

The molecule in Figure 8 is an excellent example: the equation shows that for an average \(\theta\) value of \(85.5^\circ\), \(\eta\) should be \(118.3^\circ\), whereas the average \(\eta\) value is \(119.4^\circ\); a 1.1° difference. The molecule in Figure 12 is similar: a large deviation in \(\eta\) from the extreme situation is accommodated by a value of \(\theta\) close to what is calculated from the function relating the two in an octahedral structure, as has been detailed above. This also holds true for MOP-54 in Figure 21, as detailed above. In these cases, one building block distorts slightly to adopt an angle close to that required for polyhedron formation.

There are three special cases, in which the general accommodation scheme discussed above does not hold true. The first is the tetrahedral molecule shown in Figure 6. The SBU in this case has angles \(\eta_1 = 90^\circ\), \(\eta_2 = 55.6^\circ\). The 1,3,5-tris(4-pyridylmethyl)benzene SBU in this particular conformation is very useful in that it adopts an angle \(\eta_1\) close to \(60^\circ\).

The second special case is that of the cubic molecule in Figure 15. Specifically, the second construction scheme presented shows significant deviation from the extreme angles (\(\eta = 120^\circ, \theta = 109.5^\circ\)). As discussed above, the SBU points of extension, and accordingly the linkers, are not oriented toward the edge-centers of the second extreme cube. The
octahedral coordination of the Ni atoms prevents such orientation.

Finally, the third special case is the rhombic dodecahedron in Figure 24. In this molecule, a significant deviation in η is not accommodated by a change in η. Instead, the Ni–C and Cr–N coordination vectors are not colinear. This permits the necessary flexibility for the formation of the molecule.

11. Summary and Outlook

This review provides a basis for predictable synthesis and subsequent investigation of MOPs. Both the SBUs and the linkers can be synthesized with a predetermined geometry using appropriate reaction conditions and starting materials, and the possibilities are virtually limitless. In particular, we have shown the importance of control of angles of SBUs and linkers, although we have remarked that nature is generally forgiving of small deviations from ideality. These concepts will be of increasing importance as the field of MOP reticular chemistry continues to grow. We have limited our examples, with two exceptions, to those for which explicit coordinates were available for the atoms. We have not found such examples for molecules based on icosahedral polyhedra and the preparation of these remains a nice challenge. However, in this connection, attention should be called to the elegant dodecahedral molecules reported by Olenyuk et al., for which atomic coordinates are not available. [40]

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[4] One might consider this a case of Pauling’s rule of parsimony: “the number of essentially different kinds of constituents in a crystal tends to be small”. L. Pauling, J. Am. Chem. Soc. 1929, 51, 1010.

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